INTERPRETATION OF Ar^+-Ar COLLISIONS AT 50 KeV

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Coincidence experiments on Ar^+-Ar inelastic collisions by Afrosimov et al.[1] and, still more recently, by Everhart and collaborators[2,3] are introducing us to the dynamics of interpenetrating atomic shells. This Letter intends to show how the experimental results fit into and help us to extend existing knowledge of atomic and molecular mechanics.

Specifically, we suggest, in partial disagreement with initial interpretations,[2] that (1) the gross structure of the spectrum of energy dissipation reflects the shell structure of the colliding atoms; (2) dissipation stems primarily from the electron promotion mechanism of molecular orbital theory[4,5] and is followed by autoionization; (3) the consequences of (1) and (2) can be tested by observing the spectrum of ejected electrons. As in previous work on similar problems,[6] we regard the Ar^+-Ar system as a molecular ion, Ar_2^+, and examine its independent electron molecular orbitals in the Born-Oppenheimer approximation. (The nuclear velocities are ~5 times slower than those of the outer electrons in this problem.)

The experimenters bombard Ar gas with 12- to 150-keV Ar^+ and detect pairs of emerging ions Ar^{m+} and Ar^{n+} in coincidence, measuring the rate of coincidences for each pair of charge states (m,n) and for each pair of angles of emergence ($\theta \sim 10°$, $\varphi \sim 80°$). The values of θ and φ determine (a) the distance r_0 of closest approach of the nuclei, through classical orbit theory justified by the large masses, and (b) the degree of inelasticity, i.e., the energy transfer Q from kinetic to excitation and ionization energy of the two atoms, through the energy and momentum equations. The averages of the statistical distributions of charges (m,n) and of energy loss Q increase as r_0 decreases, but depend very weakly on the collision energy for a fixed r_0. The distribution of Q shows three peaks for $r_0 \sim 0.25$ Å, whose energies are nearly constant but whose relative heights vary sharply as r_0 decreases. These features are sharpened in reference 1 by plotting, instead of Q, the kinetic energy Q^* of the ejected electrons (plus a presumably small amount of electromagnetic radiation and final metastable excitation); this is obtained by subtracting from Q the energy $U(m,n)$ required to strip the atoms to the charge levels m, n $[Q^* = Q - U(m,n)]$. The peaks of the Q^* distribution lie at ~50, 260, and 470 eV (Fig. 1).

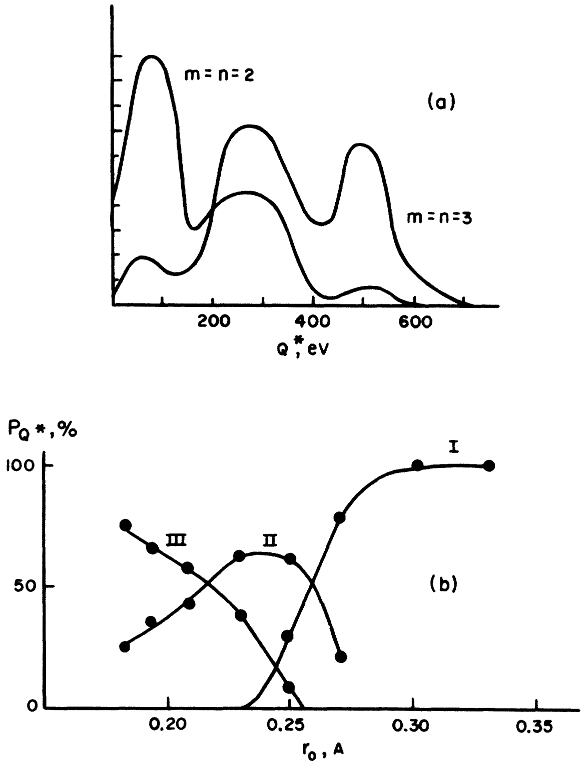

FIG. 1. Data from reference 1. (a) Q^* spectra from two classes of collisions at $r_0 = 0.25$ Å showing three peaks; the coincidence of peaks would be destroyed by a shift to the Q scale, which differs by 81 eV for the two curves. (b) Relative areas under the three peaks as a function of r_0, for $m = 2$, $n = 3$.

Here we make the suggestion, consistent with reference 3, that the three peaks of the Q^* distribution correspond to collisions in which zero, one, and two electrons, respectively, are raised out of the inner L shells of either Ar atom, in addition to a variable number of M-shell excitations. The resulting internal vacancy is normally filled by an Auger process which involves two outer electrons: One moves in and the other leaves the atom with a kinetic energy equal to the relevant L-shell ionization potential (244, 246, or 287 eV) less the M-shell double-ionization potential ($\geqslant$43 eV depending on possible preionization of the atom). This kinetic energy constitutes a rather well-defined "quantum" of ~200 eV which is clearly distinguishable over the kinetic-energy background due to M-shell processes and agrees well with the observed interval between the peaks. It is of essence that the second and then the third peaks become prominent just as r_0 decreases through the point of interpenetration of the L shells [Fig. 1(b)]. A semiquantitative estimate of the molecular levels shown in Fig. 2 confirms that extensive crossing of the M- and L-shell levels occurs at the critical values of r_0.

The level crossing may transfer an L-shell electron to an excited bound orbital, and cause, through the following Auger processes, one or more ionizations. (The presumed necessity of association of L-shell processes with double ionization contributed in reference 1 to the rejection of the present interpretation.) Note in Fig. 2 that only the two L electrons of Ar$_2^+$ in the $4f\sigma$ orbital have an opportunity to cross the M levels in the critical range $r_0 \sim 0.25$ Å $= 0.5$ a.u.; therefore only three peaks can appear in the Q^* distributions of ref. 1, whereas larger values of Q had been observed earlier[7] at $r_0 \sim 0.1$ Å $= 0.2$ a.u.

The observed distribution of Q^* within each peak appears to result from the superposition of alternative multielectron M-shell excitations, whereas reference 1 regarded each peak as the result of a single characteristic process modified by observational or minor substantive fluctuations.

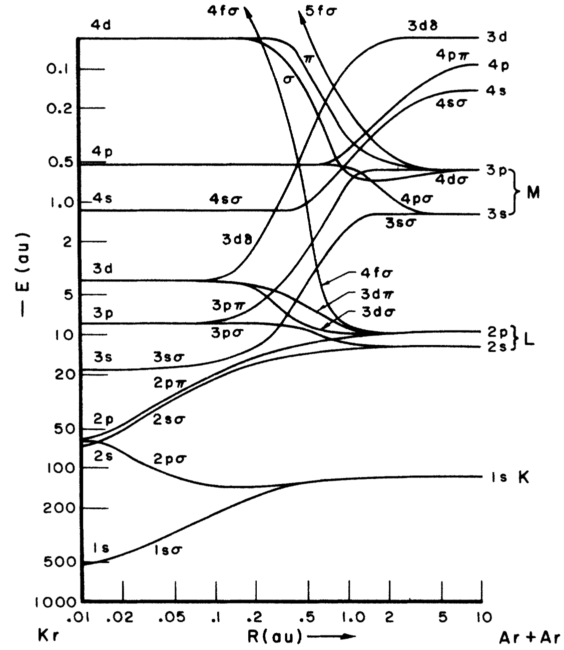

FIG. 2. Energies of diabatic molecular orbitals suitable for discussion of fast collisions between argon atoms and/or ions. A semiquantitative estimate of the energies for the H_2^+-like molecular orbitals is shown. The energies at $R=\infty$ are of the separated Ar atoms, at $R=0$ of the united Kr atom. Electron-electron interactions within the independent particle model cause transitions between diabatic molecular orbitals of like parity ($s \longleftrightarrow s$, $s \longleftrightarrow d$, $p \longleftrightarrow p$, $p \longleftrightarrow f$, etc.) and equal angular momentum λ ($\sigma \longleftrightarrow \sigma$, $\pi \longleftrightarrow \pi$, etc.). Rotational uncoupling causes transitions between molecular orbitals of like parity and $\Delta\lambda = \pm 1$ ($\sigma \longleftrightarrow \pi$, $\pi \longleftrightarrow \delta$, etc.). Electron correlation (configuration interaction) allows two-electron, or (in the case of $\lambda \neq 0$) four-electron, transitions between any pair of molecular orbitals. As the atoms approach, all these effects cause transitions of M electrons into higher shells in the vicinity of $R \sim 1$-2 a.u. In the vicinity of $R \sim 0.5$ a.u., one $4f\sigma$ electron can be transferred to $4p\sigma$ or $3p\pi$ (if the molecular orbital is not filled) or $4p\pi$; both electrons can be transferred to any orbital. At crossings at smaller R, other L electrons can be transferred to higher shells. K-shell excitation can only occur at very small internuclear distances, and is not expected under the conditions of references 1, 2, 3, and 7.

The extent of the ionization observed and, more specifically, the rapid decrease of the low-Q^* peak as r_0 enters the critical range, show that the level crossing leads with high probability to the "promotion" of electrons to outer shells, as the nuclei approach. It will be shown in a detailed paper that numerous mechanisms contribute to this promotion and cause many-electron jumps at the crossings (see Fig. 2). These transitions lead to singly or, more often, multiply excited autoionizing states in atomic collisions. Mechanisms also exist that enhance the otherwise negligible direct ionization. We emphasize that simultaneous excitations of many (say $\geqslant$4) electrons have not been considered before, and that they appear as likely results of atom, but not of electron or photon, bombardment. This type of excitation also should occur immediately after nuclear fission.

A concrete test of the present interpretation is provided by the spectrum of the ejected electrons. We predict, first, the presence of discrete energy groups which arise from inner vacancies through Auger processes. In particular, in argon there should be strong peaks in the neighborhood of 200 eV. (The prediction of the location of these peaks in other atoms is elementary.) Second, autoionization processes in outer shells should yield numerous peaks in the range ≤25 eV. This prediction of a dominant influence of the discrete structure of atomic levels contrasts with the prediction of a quasi-Boltzmann distribution, which follows from the semi-statistical model of Russek.[8] These tests should be feasible, since rich structures have already been observed in the electron spectra from H^+ and H_2^+ collisions with He, Ne, and Ar.[9]

We thank Professor Everhart for advance copies of his papers.

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